Science of the Total Environment 647 (2019) 725–733

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

One-pot synthesis of catalytic molybdenum based nanocomposite nano-fiber membranes for aerosol air remediation

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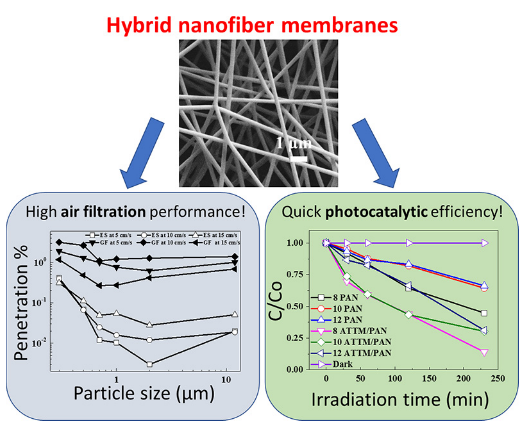
HIGHLIGHTS

- The catalytic nano-fiber membranes exhibited higher filtration efficiency compared to macro-fibrous materials
- The protrusions structures led to more lightweight membranes with higher particle capture capacities
- The samples offered higher air filtration performance than the benchmarked commercial air filters
- The photocatalytic activity of the composite ATTM/PAN membranes was two times higher than the bare PAN nanofibers

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 April 2018
Received in revised form 3 August 2018
Accepted 4 August 2018
Available online 04 August 2018

Editor: Jianmin Chen

Keywords:
Electrospinning
Air filtration
Photocatalytic membranes
Nano-composite nanofibers
Self-cleaning membranes

ABSTRACT

The development of fibrous air filters exhibiting high air filtration efficiency, low energy consumption, and self-cleaning properties is a critical challenge to generate the next generation of resilient air filtration systems. Nano-fibrous mats typically exhibit higher particle capture efficiency but may also lead to higher airflow resistance compared to macro-fibrous materials due to their tighter structure. In this paper, novel catalytic membranes mats were fabricated through a one-pot synthesis from ammonium tetrathiomolybdate (ATTM) doped poly(acrylonitrile) (PAN) nanofibers for sub-micron diameter aerosol particle removal. The presence of ATTM as a dopant in conjunction with a PAN polymeric matrix was found to not only enhance the air filtration performance by increasing aerosol particle removal down to 300 nm, but also increase the photocatalytic properties of the PAN material. The enhanced separation properties compared to bare polymeric PAN nanofibrous membranes were attributed to surface nanotexturation of the fibers, leading to protrusions and pores across the nano-fiber structures, thus leading to more permeable and lightweight membranes with higher particle capture capacities. The samples were benchmarked against commercial glass fiber air filters and found to offer higher filtration efficiency, lower pressure drop, and higher quality factor than the commercial filters. Specifically, the quality factors of the catalytic nano-fiber membranes were found to be up to four times higher than that of the benchmarked

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https://doi.org/10.1016/j.scitotenv.2018.08.050

commercial air filters for $PM_{2.5}$ particles, while two times higher for 300 nm sized contaminants. The presence of the ATTM across the PAN matrix was also found to enhance the photocatalytic activity of the membranes by up to 130% compared to the bare PAN reference nanofibers. This novel strategy opens avenues to engineering advanced multifunctional catalytic membranes, to capture toxic particulate matter from air while offering self-cleaning properties when exposed to sunlight.

1. Introduction

The World Health Organization (WHO) reported in 2017 that ~92% of the world population is exposed to air quality levels below the recommended limit, while >11% of the global deaths may be directly related to indoor and outdoor air pollution sources (World Health Organization, 2016).

Particulate matter (PM) is the main cause for these deaths and is typically a complex mixture of harmful airborne pollutants. On the one hand, PM $_{2.5}$ particles, which have an average size in the vicinity of 2.5 μm, are among the widespread contaminants able to diffuse nearly unimpeded into bronchi and lungs. $PM_{2.5}$ particles are often by-products of combustion and are present e.g. as fly-ash dusts across most metropolitan areas (Pope and Dockery, 2006). On the other hand, particles smaller than 500 nm, typically formed by clustering of anthropogenic nanomaterials like diesel soot, represent aerosols of the most penetrating particle size (MPPS) distribution for typical commercial air filters due to their low weight and ability to diffuse by Brownian motion (Podgórski et al., 2006).

Efforts have been dedicated to offering sustainable remediation solutions to capturing such air pollutants and membranes filtration systems are nowadays the most promising new technologies for both personal filters and industrial scale aerosol suppression (Al-Attabi et al., 2018a). The diameter distributions of the fibers, and the overall resulting pore size distributions, are pivotal factors in the design of air filtration membranes and must be carefully optimized to the specific target applications (Zhu et al., 2017). Membranes composed of nanofibers were however shown to exhibit higher particulate capture capabilities compared to conventional micro-sized fibers (Zhao et al., 2016).

Although the potential of nanofiber-based membranes has been widely demonstrated in the area of air filtration a major challenge to their utilization related to the high pressure drop across these materials remains. The pressure drop is due to the higher levels of densification upon compaction under air pressure compared to commercial membranes (Wang et al., 2014; Wang et al., 2015; Mao et al., 2016; Wan et al., 2014; Al-Attabi et al., 2018b; Zhang et al., 2017; Al-Attabi et al., 2018c). Although electrospun membranes offer uniform fiber diameter and size distributions, promising high-precision material solutions towards tuneable pore size and porosity control, in addition to facile blending with other materials to generate composite nanofibers with synergistic properties, their application remains hindered due to typically higher operating pressure drops and lower quality factors compared to commercial membranes (Al-Attabi et al., 2018b; Al-Attabi et al., 2018c; Yun et al., 2010; Balgis et al., 2015). The resulting pressure drop across electrospun membranes is also often higher than that from benchmark commercial air filters due to the lower resistant to compaction of nanofiber based mats, which leads to prohibitive operational costs and energy consumption (Al-Attabi et al., 2018b; Al-Attabi et al., 2018c; Barhate et al., 2006; Wang et al., 2008). This challenge must therefore be tackled to develop cost-effective electrospun air membranes and to benefit from the promising capture mechanisms offered by such nanofiber materials.

A number of polymeric materials have been successfully electrospun for air filtration application, including polyacrylonitrile (PAN) (Al-Attabi et al., 2018b; Al-Attabi et al., 2018c), poly(lactic acid) (PLA) (Wang and Pan, 2015), polyamide (PA) (Vitchuli et al., 2010), polyurethane (PU) (Sambaer et al., 2012; Scholten et al., 2011), polyethylene oxide (PEO) (Chang and Chang, 2016), polyvinyl alcohol (PVA) (Li et al., 2015; Wang et al., 2010), polyamide 6/6 (PA6/6), polyamide (PA6), polyvinyl acetate (PVAc), cellulose acetate (CA) (Matulevicius et al., 2016), and polyvinylidene fluoride (PVDF). Among them, PAN, a weather resistant conjugated polymer, offers a large dipole moment with unique photocatalytic properties (Liu et al., 2015; Su et al., 2017; Yar et al., 2017). Such photocatalytic properties may be leveraged by designing nanocomposite fibers with enhanced electron diffusion properties at the polymer - dopant interfaces (Yar et al., 2017). The photocatalytic properties are there induced by absorption of light via generation and recombination of the electrons and holes (Yar et al., 2017). The impact of the dopant materials on the air filtration performance, including the filtration efficiency, pressure drop, and quality factor, are highly related to synergistic interactions with the structural properties of the electrospun nanofiber polymer.

Herein, a one-pot synthesis of catalytic nano-fiber mats for the removal of nano-scale aerosols in air is demonstrated for the first time from Ammonium tetrathiomolybdate (ATTM) doped nano-composite PAN nanofiber membranes. The impact of the fibers and membranes properties were systematically correlated to the web structure and capture/decomposition performance of the electrospun nanofiber membranes. Furthermore, air filtration performance of the electrospun membranes were investigated and benchmarked against commercial air filters and bare electrospun PAN membranes. The ATTM doping within the polymeric matrix was found to improve the bare PAN air filtration performance, both in terms of capture capacity and pressure drop making such ATTM/PAN nano-composite fibers extremely promising and resilient air filtration materials. Finally, the photocatalytic performance of the nano-composite electrospun membranes were assessed through the degradation of a probe dye molecule adsorbed on the surface of the fibers, demonstrating for the first time self-cleaning properties. These are critical features for photocatalysis and could be used to remediate fouling or degrade toxic contaminants from waste waters, biological wastewater treatment (Huang et al., 2016; Shi et al., 2017), and outdoor filtration applications where high levels of volatile organic compounds are present.

2. Experimental

2.1. Materials

Poly(acrylonitrile) (PAN) (Mw 150,000 g/mol) powder, Ammonium tetrathiomolybdate (ATTM) powder, *N N* dimethylformamide (DMF) (99.8% purity) were used for the synthesis of the polymeric dope spinning solution; while Rhodamine 6G (R6G) served as indicator for the catalytic tests and potassium chloride (KCl) (99.9% purity) was used to generate the aerosol particles. All chemicals were purchased from Sigma-Aldrich and used as received without further treatments.

2.2. Fabrication of ATTM/PAN composite nanofiber membranes

ATTM/PAN/DMF precursor solutions were prepared by dissolving of 30% of ATTM with respect to PAN concentration in DMF and stirred